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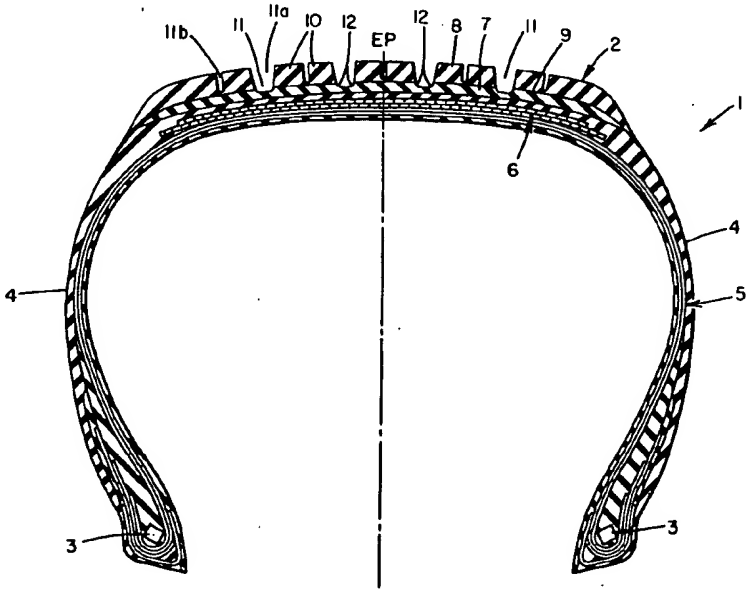
(54) **Tire with dual cap tread.**

(57) A tire having a tread of a dual cap construction where the cap rubber is comprised of an inner and outer layer where said inner cap layer is comprised of at least one selected diene rubber and a trans 1,4-polybutadiene rubber.



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Field

This invention relates to a pneumatic rubber tire having a rubber tread of a dual cap construction. More specifically, the invention relates to such a tire having a tread cap of inner and outer elastomeric compositions.

The invention is particularly applicable to a relatively thick tire tread with relatively deep grooves as may be found, for example, on truck tires.

Background

Truck tires conventionally have relatively thick treads and correspondingly relatively deep grooves. Exceptional stress is often transmitted to the bottom, or inner region, of the deep grooves because of the leverage and bending moment administered by the high walls of the tread lugs associated with the grooves.

Such stress can cause the surface of the grooves, near their bottom, to crack, particularly when the tire is being used under relatively heavy service conditions. Such groove cracking at the inner region of the grooves is not normally desirable because of an undesirable appearance and also because such cracks could propagate, become larger, and trap water, dirt and road debris, with various attendant difficulties.

Typically, the outer cap portion of the tread contains the visible tread grooves and associated lugs, or raised portions, which is designed to contact the ground. The cap portion usually includes such tread configuration and usually extends to a tread depth of just below the grooves of the tread. The rubber for the cap portion is often compounded to provide good skid resistance, treadwear and rolling resistance for the tire.

Sometimes the tread is also provided with a base portion positioned beneath the cap portion and, being a part of the tread itself, is located between the tread cap and an underlying supporting belt or carcass portion of the tire. However, it is the cap portion that contains the lugs and groove configuration of the tread. Such tire construction is well known.

A tread cap composed of dual layers of rubber has been proposed. The outer layer would be expected to contact the road and the inner layer, adjacent to the carcass or tread base, as the case may be, would be designed to counteract or reduce the aforesaid groove cracking. Such inner layer of the tread cap would include the inner region of the aforesaid tread grooves, at least the deep grooves of the tread.

Accordingly, it is envisioned that the inner cap layer is an inward extension of the outer cap layer rather than outward extension of a tire carcass portion or tread base layer, as the case may be.

The use of trans 1,4-polybutadiene for various purposes has been disclosed, including, for example, tire tread rubber compounds (See, for example, Japanese Patent Publication Nos. 60-133,036; 62-101,504 and 61-143,453) and U.S. Patent Nos. 4,510,291 and 5,025,059. It has been proposed to use trans 1,4-polybutadiene as a component of the base of a tread cap/base construction.

However, in this application, the requirements for the inner cap layer are more similar to and aligned with those of the outer cap layer (treadwear, skid resistance, etc.) instead of a base of a tread of a cap/base construction. This is because as the tire tread wears, the inner cap portion is expected to eventually become exposed to road surface and require roadwear and traction properties, similar to the outer cap portion, which are requirements not normally required of the tread base component of the tread, which is not normally intended to be the road contacting part of the tire.

Uniquely, trans 1,4-polybutadiene is typically a thermoplastic resin rather than rubber in its uncured state at room temperature by virtue of its high crystallinity. Because it contains many double bonds in its backbone, it can, however, be suitably blended and co-cured with elastomers.

Disclosure and Practice of the Invention

In accordance with this invention, a rubber tire is provided having a rubber tread of a dual cap construction with lugs and associated grooves therein, where said cap is comprised of an inner cap layer and an outer cap layer adapted to be ground contacting; where said outer cap layer encompasses at least 25 percent, preferably a major portion, and more preferably about 75 to about 85 percent of the outer depth of the deepest tread grooves; and where said inner cap layer encompasses up to about 75 percent, preferably a minor portion and more preferably about 15 to about 25 percent of the inner depth of the deepest tread grooves; and where said inner cap layer underlies and extends beneath all of the tread grooves; wherein said inner cap layer is a sulfur cured rubber layer composition comprised of, based on 100 parts by weight rubber (phr), (A) about 40 to about 95, preferably about 50 to about 80 parts by weight of at

least one diene rubber selected from natural and/or synthetic cis 1,4-polyisoprene rubber, cis 1,4-polybutadiene rubber, styrene/butadiene copolymer rubber, styrene/isoprene/butadiene terpolymer rubber and 3,4-polyisoprene rubber; and (B) about 5 to about 60, preferably about 20 to about 50 parts by weight of a trans 1,4-polybutadiene characterized by having about 75 to about 85 percent trans 1,4-content.

In the description of the tread cap of this invention, in one aspect the outer cap layer is described as being a major portion of the tread cap and, correspondingly, the inner cap layer being of a minor portion. This reference is used in a conventional sense in that it is intended that the outer cap layer thickness be more than 50 percent (e.g. at least 51 percent) of the tread cap thickness and, correspondingly, that the inner cap layer be of a minor portion or less than 50 percent (e.g. up to 49 percent) of the overall cap thickness, as measured from the outer tread surface to the "bottom" of the tread cap which extends beneath the tread grooves.

Further, the tread grooves are conveniently referenced as to their outer portions (for the outer cap layer) and inner portions (for the inner cap layer). The outer portion of the grooves typically communicate directly with the outer, exposed surface of the tread and the inner portions extend to the bottom of the grooves.

In one aspect, the outer and inner cap layers are described as encompassing the respective groove portions in that they are actually a part of the walls of the grooves.

The outer cap layer is described as being adapted to be ground contacting in a sense that it is intended that it is the surface of the tire tread which is intended to be in contact with a substrate (e.g. ground) over which the tire is intended to travel.

Preferably, such trans 1,4-polybutadiene is characterized by having about 75 to about an 85 percent of its butadiene repeat units of a trans 1,4-isomeric structure, about 2 to about 18 percent of its units of a 1,2-structure and about 2 to about 18 percent of its units of a cis 1,4-structure and, in its uncured state, at least one melting point in the range of about 35°C to about 60°C.

In one aspect of the invention, the outer cap portion is a sulfur cured rubber composition exclusive of trans 1,4-polybutadiene. Thus, in such aspect, the outer cap portion does not contain trans 1,4-polybutadiene.

For the purposes of this description, the "compounded" rubber compositions refer to the respective rubber compositions which have been compounded with appropriate compounding ingredients such as, for example, carbon black, oil, stearic acid, zinc oxide, silica, wax, antidegradants, resin(s), sulfur and accelerator(s).

In the practice of this invention, the said tread cap may have an overall thickness in a range of about 6.5 to about 25 millimeters, with the outer cap layer having a thickness of about 4.5 to about 20 millimeters and the inner cap layer having a thickness of about 2 to about 20.5 millimeters. While these thickness may be considered as being representative for descriptive purposes, individual tread thickness may vary from tire to tire, depending somewhat upon the tire size and its intended service conditions.

Indeed, for large off-the-road and large agricultural tires, the overall tread cap thickness may be even up to about 140mm, and said inner cap layer has a thickness of up to 35mm or more.

While the grooves in any tire tread, between associated lugs, may be of a multitude of depths, the deepest grooves may have a depth of about 5.5 to about 22 millimeters, which is a measure of the height of their walls. Preferably, about 15 to about 25 percent or, if the tires intended service warrants, up to 75 percent, of the depth of the deepest grooves are contained by the said inner cap rubber layer, whereas the shallowest grooves may be completely contained in the outer cap portion, again depending on the type and intended service of the tire.

Thus, in one aspect of the invention, a tread of said dual cap construction is provided where up to about 75 percent of the depth of the tread's deepest grooves are encompassed by the said inner cap layer. In a preferred aspect, about 15 to about 25 percent of the depth of the tread's deepest grooves are encompassed by the inner cap layer.

The inner cap layer is not considered to be simply an extension of a tire carcass or a tread base layer of a tire or a tire tread's cap/base construction. This is because the inner cap layer now actually contains the lower tread groove region, whereas a tread base is conventionally considered to basically exclude the tread grooves. Also, the desired physical properties for the inner cap layer, such as, for example, treadwear, cut growth resistance, tear and flex fatigue resistance, more closely approximate the desired properties for the outer cap layer rather than for a base layer in a tread cap/base construction or a tread supporting tire carcass, as the case may be.

The trans 1,4-polybutadien utilized by this invention might be prepared, for example, by anionic polymerization batch or continuous of 1,3-butadiene in an organic solvent and in the presence of cobalt octoat and triethyl aluminum as a catalyst system with a para alkyl substitut d phenol as a catalyst modifier.

The trans 1,4-polybutadien , in its uncured state, has been observed to xhibit at least one softening or melting point.

In th practice of this invention, the outer tread cap layer rubber composition may be comprised of at least on rubber selected, for example, from at least on of cis 1,4-polyisoprene rubber, both natural and synthetic, 3,4-polyisoprene rubber, styrene/butadiene copolymer rubbers, styrene/isoprene/butadiene terpolymer rubbers, and cis 1,4-polybutadiene rubber. Preferably it is comprised of a combination of natural rubber or cis 1,4-polyisoprene rubber and cis 1,4-polybutadiene rubbers. In one aspect, the outer cap layer is exclusive of trans 1,4-polybutadiene.

A base rubber composition, if used in combination with and underlying the cap inner rubber layer, may be, for example, comprised of various sulfur curable rubbers such as, for example, 1,4-polyisoprene rubber, natural or synthetic 1,4-polybutadiene rubber and styrene/butadiene copolymer rubber. It one aspect, it may contain trans 1,4-polybutadiene.

It is readily understood by those having skill in the art that the rubber compositions of the inner and outer cap rubbers would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

Typical additions of carbon black comprise about 20 to 100 parts by weight of diene rubber (phr), preferably 30 to 60 phr. Typical amounts of tackifier resins, if used, comprise about 0.5 to about 10 phr, usually about 1 to about 5 phr. Typical amounts of processing aids may comprise 1 to 20 phr. Such processing aids can include, for example, aromatic, napthenic, and/or paraffinic processing oils. Silica, if used, may be used in an amount of about 5 to about 25 phr, often with a silica coupling agent. Representative silicas may be, for example, hydrated amorphous silicas. Typical amounts of antioxidants may comprise about 1 to about 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in the Vanderbilt Rubber Handbook - (1978), pages 344-346. Typical amounts of antiozonants comprise about 1 to about 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise about 0.5 to about 3 phr. Typical amounts of zinc oxide comprise about 2 to about 5 phr. Typical amounts of waxes comprise about 1 to about 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise about 0.1 to about 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide. The presence and relative amounts of the above additives are considered to be not an aspect of the present invention which is more primarily directed to the utilization of specified blends of rubbers in tire treads.

The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from about 0.5 to about 4 phr, with a range of from about 1.5 to about 2.25 being preferred.

Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally, a primary accelerator is used in amounts ranging from about 0.5 to about 2.0 phr. In another embodiment, combinations of two or more accelerators which is generally used in the larger amount (0.5 to 1.0 phr), and a secondary accelerator which is generally used in smaller amounts (0.05-0.50 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators have been known to produce a synergistic effect of the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce satisfactory cures at ordinary vulcanization temperatures. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound. The presence and relative amounts of sulfur vulcanizing agent and accelerator(s) are not considered to be an aspect of this invention which is more primarily directed to the utilization of specified blends of rubbers in tir treads, particularly the inclusion of th trans 1,4-polybutadiene in th tread inner cap lay r.

The tir can b built, shaped, molded and cured by various methods which will be readily apparent to thos having skill in such art.

The prepared tire of this invention is conventionally shaped and cured by methods known to thos having skill in such art.

For a further understanding of the invention, reference is made to the accompanying drawing.

Referring to the drawing, a cross-section of a radial ply pneumatic rubber tire 1 is shown.

The tire 1 is comprised of a tread 2, two beads, or bead elements 3, sidewalls 4 abridging said tread 2 and bead elements 3 and a belt 6 and ply 5 for supporting said tread 2 and sidewalls 4. This is considered to be a description of a somewhat conventional radial ply pneumatic rubber tire.

In accordance with this invention, the tread 2 is represented as a cap element which itself is divided into an inner cap portion, or layer, 7 and an outer cap portion, or layer, 8. A dividing line 9 is shown, for convenience, between the inner cap portion 7 and outer cap portion 8.

The tread 1 is also configured with lugs 10 and grooves 11. While such grooves 11 may be of various depths, for illustration purposes, relatively deep grooves 11a and shallow grooves 11b are depicted.

Also pointed out for the deep grooves 11b are their inner, bottom, or base, radii 12 located at the bottom of the grooves 11.

A review of the drawing shows that the inner cap portion 7 extends outward and encompasses at least a portion of the depth of the deepest grooves 11b as is more clearly shown by the dividing line 9.

The inner cap portion 7 also underlies and extends beneath all of the grooves 11 of the overall tread cap 2.

As indicated in this specification, the inner cap portion 7 contains the trans 1,4-polybutadiene and is designed to retard or substantially eliminate the cracking of the deep grooves 11b encompassed by the inner cap portion 7, particularly at their inner radii 12.

The outer cap layer 8 encompasses a major portion of the outward extension of the lugs 10 and associated grooves 11 and particularly 11b.

The invention may be better understood by reference to the following example in which the parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Mixtures of diene rubbers with trans 1,4-polybutadiene having two softening points of about 40 °C and 60 °C, in its uncured state, were prepared comprised of the following recipe shown in Table 1 as Experiments A, B and C. Experiment A is considered a control.

Table 1

Material	Parts Exp A (Control)	Parts Exp B	Parts Exp C
Natural rubber/or cis 1,4-polyisoprene rubber	100	60	60
Cis 1,4-polybutadiene rubber	0	20	40
Trans 1,4-polybutadiene	0	20	0
Carbon black (N100 series)	46	46	46
Processing oil, wax, zinc oxide, and stearic acid	6.5	6.5	6.5
Antidegradants	2.5	2.5	2.5
Accelerator	1.1	1.1	1.1
Sulfur	1.5	1.5	1.5
Retarder	0.2	0.2	0.2

Conventional, amounts of antidegradant(s) (paraphenylene diamine type), zinc oxide, stearic acid, accelerator of the sulfenamid typ wer used.

1. A trans 1,4-polybutadien for this inv ntion characterized by high trans 1,4-polybutadi n content (80 percent trans 1,4-).

Th trans 1,4-polybutadiene for this exampl was charact riz d by having a trans 1,4-content of about 80 percent, a cis 1,4-cont nt of about 5 percent and a vinyl 1,2-content of about 15 percent. It was further

characterized by having an number averag molecular weight (Mn) of about 205,000 and a weight av rag molecular weight (Mw) of about 430,000. It was additionally charact rized by having a Tg of about -75°C and m lting points (Tm) of 40°C (major) and 60°C (minor). (Both the Tg and Tm can be determined by differential scanning calorimeter at 10°C per minute).

Such trans 1,4-polybutadiene can be suitably prepared by batch polymerizing 1,3-butadiene in an aliphatic hydrocarbon solution (e.g. hexane) in the presence of a catalyst of cobalt octoate and triethylaluminum with p-dodecylphenol modifier, although it can also be prepared by continuous polymerization with a suitable gel inhibitor.

EXAMPLE II

The prepared rubber compositions were cured at a temperature of about 150°C for about 20 minutes and the resulting cured rubber samples evaluated for their physical properties as shown in the following Table 2. The experimental samples A, B and C correspond to the experimental samples A, B and C of Example I.

Cured sheets or strips were prepared for each of samples A, B and C for modulus, tensile and elongation tests; for rebound test, for tear test and for the belt crack test. The samples for the belt crack test contained a multiplicity of grooves with various widths and depths.

Table 2

Properties	Exp A (Control)	Exp B	Exp C
300% Modulus (MPa)	10.7	9.6	10.6
Tensile (MPa)	22.9	21.2	20.1
Elongation (percent)	498	489	456
Rebound (23°C)	48.8	55.4	56.7
Tear (23°C) (Strebler adhesion)[1] (N)	235	261	211
Belt crack test[2]			
(a) days[3]	13	15	15
(b) appearance[4]	10	2	2

1. A test of adhesion to itself involving pulling strips apart at a 180° angle (5 mm wide strips), measured in Newtons of force.

2. (ASTM test No. D430)

3. Number of days over which the test was run.

4. A visual evaluation with a rating of 10 being the worst (deep cracks across the sample in virtually all bottom groove radii) and 1 being best (none of such groove cracking).

Thus, the tear resistant property and the resistance to fatigue cracking of the cured rubber are significantly higher for Exp. B. Thus, the trans 1,4-polybutadiene is considered an excellent candidate for the inner cap layer in a tread with a dual cap rubber.

Whil certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

Claims

1. A rubber tire having a rubber tread of a dual cap construction with lugs and associated grooves therein, where said cap is comprised of an inner cap layer and an outer cap layer adapted to be ground contacting; characterized in that said outer cap layer contains at least 25 percent and up to about 85 percent of the outer depth of the deepest tread grooves; and where said inner cap layer encompasses up to about 75 percent of the inner depth of the deepest tread grooves, and where said inner cap layer underlies and extends beneath all of the tread grooves; and further characterized in that said inner cap layer is a sulfur cured rubber layer composition comprised of, based on 100 parts by weight rubber (phr), (A) about 40 to about 95, preferably about 50 to about 80 parts by weight of at least one diene rubber selected from natural and/or synthetic cis 1,4-polyisoprene rubber, cis 1,4-polybutadiene rubber, styrene/butadiene copolymer rubber, styrene/isoprene/butadiene terpolymer rubber and 3,4-polyisoprene rubber; and (B) about 5 to about 60, preferably about 20 to about 50 parts by weight of a trans 1,4-polybutadiene characterized by having about 75 to about 85 percent trans 1,4-content.

2. The tire of claim 1 characterized in that said outer cap layer is of a rubber composition exclusive of trans 1,4-polybutadiene.

3. The tire of claim 2 characterized in that about 15 to about 25 percent of the depth of the tread's deepest grooves is encompassed by the said inner cap layer.

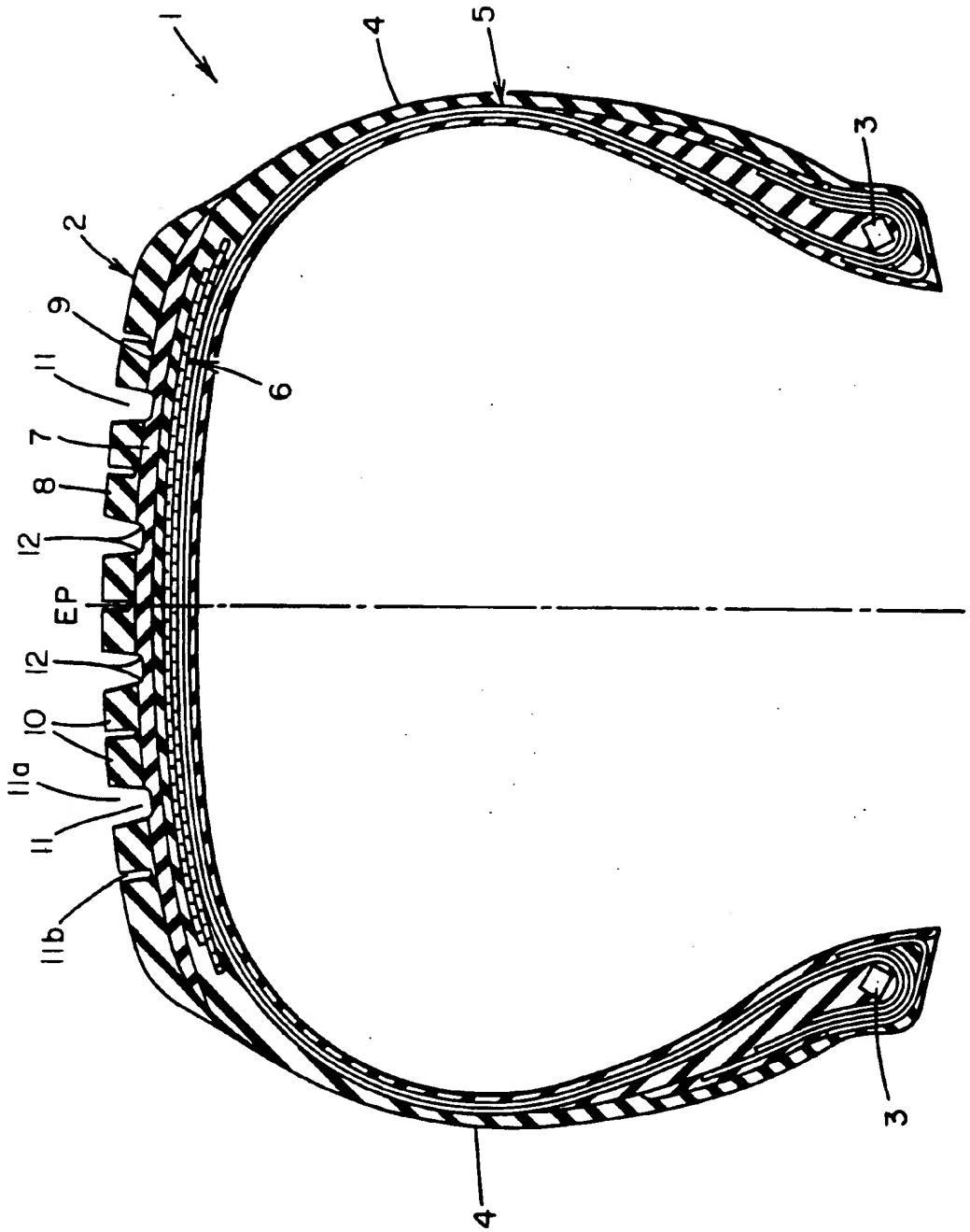
4. The tire of claim 2 characterized in that a minor portion of the depth of the tread's deepest grooves is encompassed by the said inner cap layer.

5. The tire of claim 4 characterized in that the tread cap has an overall thickness of about 6.5 to about 25 millimeters, with the outer cap layer having a thickness of about 4.5 to about 20 millimeters and the inner cap having a thickness of about 2 to about 20.5 millimeters.

6. The tire of claim 2 characterized in that the overall tread cap thickness is up to about 140mm and said inner cap layer has a thickness of up to 35mm.

7. The tire of claim 2 characterized in that the said trans 1,4-polybutadiene is characterized by having about 75 to about an 85 percent of its butadiene repeat units of a trans 1,4-isomeric structure, about 2 to about 18 percent of its units of a 1,2-structure and about 2 to about 18 percent of its units of a cis 1,4-structure and, in its uncured state, at least one melting point in the range of about 40 °C to about 60 °C.

8. The tire of claim 2 characterized in that the said outer cap layer is comprised of at least one rubber selected from at least one of cis 1,4-polyisoprene rubber, both natural and synthetic, 3,4-polyisoprene rubber, styrene/butadiene copolymer rubber, styrene/isoprene butadiene terpolymer rubbers, and cis 1,4-polybutadiene rubber.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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 7527

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 505 904 (GOODYEAR TIRE & RUBBER CO.) * abstract * * page 3, line 49 - line 53 * * page 4, line 50 - page 5, line 24 *	1,2,7,8	B60C1/00 B60C11/00 C08L21/00 //(C08L21/00, 9:00)
A	EP-A-0 098 353 (CONTINENTAL AG) * abstract; figure 1 * * page 4, line 6 - line 9 *	1-8	
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 231 (M-506)(2287) 12 August 1986 & JP-A-61 064 503 (SUMITOMO RUBBER IND KK) 2 April 1986 * abstract; figure *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C08L
B60C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 JANUARY 1993	METTLER R.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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D : document cited in the application
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